CHAPTER III

LITERATURE REVIEW

The use of group 4 metallocene complexes as homogeneous Ziegler-Natta catalysts is well established for the polymerization of olefins. In comparison with traditional Ziegler-Natta catalysts, the homogeneity of the active site and the tailorability of this new generation of catalysts markedly promote the stereospecific polymerization of α-olefins, offer unprecedented control over the properties of polymeric products, and sometimes produce new macromolecules.

Ishihara and coworkers reported in 1986 that a new macromolecule, syndiotactic polystyrene (SPS), could be produced with high stereoregularity and yields under conventional conditions with organic or inorganic titanium activated with methylaluminoxane (MAO). (η^5-cyclopentadienyl)trichlorotitanium (CpTiCl$_3$) was the most active precursor. Since then, there has been great interest in the synthesis of homogeneous organometallic complexes able to provide an efficient and stereoregular polymerization of styrene. The polymerization mechanism and the structure of the active site were investigated. Half - sandwich titanocenes containing Cp or Ind activated with MAO showed high activities. More efforts were devoted to the synthesis of new kinds of half-sandwich titanocenes and the elucidation of the relationship of the precursor structure and its catalytic behavior. Basicity, steric effects, and chirality of the ligands attached to the group 4 metal centers strongly influenced the polymerization.

3.1 Titanocenes

Ishihara *et al.* [5] found that a mixture of titanium compound (TiCl$_4$, Ti(OEt)$_4$, or CpTiCl$_3$) with methylaluminoxane catalyzes the polymerization of styrene, even above room temperature, to the pure syndiotactic polystyrene, which has molecular weight distribution (M_w/M_n) of 2. Pure syndiotactic polymers are also obtained with

ring-substituted styrenes, Monomer reactivity is enhanced by electron releasing substituents on the aromatic ring.

Fan *et al.* [56] studied powdery syndiotactic polystyrene (SPS) synthesized in a bulk process with the homogeneous metallocene catalyst system, (η^5-pentamethylcyclopentadienyl) titanium trichloride/methylaluminoxane/triisobutyl aluminum. The morphology of the nascent polymer particles were investigated. The crystallinities of the as-polymerized polymer samples at different conversions were also studied. The experimental results suggested that manipulating the relative crystallizing rate to exceed the relative polymerizing rate in the initial stage of the polymerization is feasible to prepare the powder product.

Flores *et al.* [57] synthesized and tested a series of monocyclopentadienyltitanium complexes containing the 1-(2-phenylethyl)-2,3,4,5-tetramethylcyclopentadienyl ligand ($C_5Me_4CH_2CH_2Ph$) (1). The reaction of $C_5Me_4(SiMe_3)CH_2CH_2Ph$ (2) with $TiCl_4$ was used to synthesize the trichloro complex ($C_5Me_4CH_2CH_2Ph)TiCl_3$ (3), the molecular structure of which was confirmed by an X-ray diffraction study. Complex (3) was further converted into ($C_5Me_4CH_2CH_2Ph)TiMe_3$ (4). Reaction of the latter with 1 equivalent of $[Ph_3C][B(C_6F_5)_4]$ was almost quantitative to give the "cationic" complex $[(C_5Me_4CH_2CH_2Ph)TiMe_2][B(C_6F_5)_4]$ (5). Complex (5) was thermally unstable in solution and very moisture sensitive. Complex (4) was readily hydrolyzed to $[(C_5Me_4CH_2CH_2Ph)TiMe_2]_2(\mu\text{-O})$ (6) upon recrystallization in wet pentane. Structural data indicate intramolecular coordination of the phenyl group to titanium in complex (5), whereas there are no such indications for complex (3), (4), or (6). The catalytic performance for styrene polymerization of complex (3) activated with methylaluminoxane (MAO) was compared with the nonsubstituted reference complex ($C_5Me_5)TiCl_3$ (7). Complex (5), prepared *in situ* by reacting complex (4) with $[Ph_3C][B(C_6F_5)_4]$, has also been found to be active for the syndiospecific polymerization of styrene. The polymerization data for complexes (3) and (5) lead to the tentative suggestion that the active species is in equilibrium between two states, one with and one without intramolecular phenyl coordination to Ti. This finding would be consistent with postulated multihapto coordination of

styrene by both the vinylic double bond and the aromatic ring to the metal center during the catalytic process.

Kim *et al.* [58] synthesized and tested five substituted indenyltrichlorotitanium complexes, characterized by spectroscopic methods and their catalytic behavior for the polymerization of styrene in the presence of methylaluminoxane (MAO). Substituted indenyl ligands include 1, 3-dimethyl, 1-methyl, 1-ethyl, 1-isopropyl and 1-(trimethylsilyt)indenyl groups (Figure 3.1). All five complexes gave pure syndiotactic polystyrene, with conversion rates of at least 95%, and their catalytic properties were compared with that obtained from the (η^5-indenyl)trichlorotitanium-MAO system. The catalytic activity is enhanced by less bulky and better electron releasing substituents of the indenyl ligands. The catalytic activity increases in the order of (5) < (4) ~ (3) ~ (6) < (2) < (1).
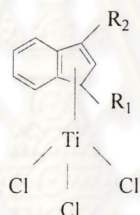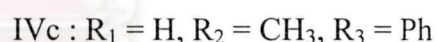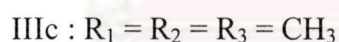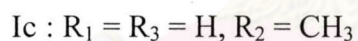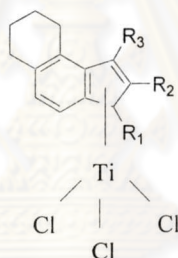

(1)	$R_1 = CH_3$; $R_2 = CH_3$	(4)	$R_1 = CH(CH_3)_2$; $R_2 = H$
(2)	$R_1 = CH_3$; $R_2 = H$	(5)	$R_1 = SiMe_3$; $R_2 = H$
(3)	$R_1 = CH_2CH_3$; $R_2 = H$	(6)	$R_1 = H$; $R_2 = H$

Figure 3.1. Substituted indenyltrichlorotitanium compounds.

Schwecke and Kaminsky [59] synthesized benzyl cyclopentadienyl titanium trichloride ($BzCpTiCl_3$) from benzyl bromide, cyclopentadienyl lithium, and titanium tetrachloride and used in combination with methylaluminoxane (MAO) for the syndiotactic polymerization of styrene. Kinetic measurements of the polymerization were carried out at different temperatures. The polymerization with $BzCpTiCl_3$/MAO differs from the polymerization with $CpTiCl_3$/MAO in its behavior toward the Al/Ti ratio. In addition, high activities are observed at high Al/Ti ratios. By analyzing the polymerization runs and the physical properties of the polymers with differential scanning calorimetry, ^{13}C NMR spectroscopy, wide-angle X-ray scattering

measurements, and gel permeation chromatography, it was found that the phenyl ring coordinates to the titanium atom during polymerization.

Xu and Cheng [60] studied the effective catalyst precursor for syndiospecific styrene polymerization, namely [2-Me-thBenz[e]Ind]TiCl$_3$ (Ic), [2,3-Me$_2$-thBenz[e] Ind]TiCl$_3$ (IIc), [1,2,3-Me$_3$-thBenz[e]Ind]TiCl$_3$ (IIIc), [2-Me-3-Ph-thBenz[e]Ind]TiCl$_3$ (IVc) and examined the influence of ligand pattern on the catalyst activity and polymer properties. Of all titanocenes examined (Figure 3.2), [2-Me-3-Ph-thBenz[e] Ind]TiCl$_3$ (IVc)/MAO showed the highest activity at low Al/Ti ratio of 1000, revealed the excellent control over the stereoregular insertion of monomer, and exhibited a significant increase of the ratio of the propagation rate to chain transfer termination as evidenced by the kinetic results (Table 3.1). The EPR spectrum showed that the higher activity of tetrahydrobenz[e]indenyl-based systems is due to a great number of active species.

Ic : R$_1$ = R$_3$ = H, R$_2$ = CH$_3$ IIc : R$_1$ = H, R$_2$ = R$_3$ = CH$_3$

IIIc : R$_1$ = R$_2$ = R$_3$ = CH$_3$ IVc : R$_1$ = H, R$_2$ = CH$_3$, R$_3$ = Ph

Figure 3.2. Substituted tetrahydrobenz[e]indenyl trichlorotitanium compounds.

Table 3.1. Syndiotactic polymerization of styrene using methylaluminoxane activated half sandwich titanocene

titanocene	Yield (g)	Activity ($\times 10^{-7}$)	% SPS	T_m (°C)	M_w ($\times 10^{-5}$)	M_w / M_n
Ic	7.5	13.61	95.2	270	0.95	2.1
IIc	7.0	12.70	96.1	272	1.79	2.0
IIIc	4.3	7.80	97.5	272	2.56	2.3
IVc	8.0	21.77	98.1	275	6.57	2.0

Activity = (g of PS)/[(mol of Ti) (mol of styrene) h]

Ma *et al.* [61] synthesized $CpTiCl_2(OR)$ alkoxyl-substituted half-sandwich complexes, where R was methoxyethyl (1), methoxypropyl (2), methoxyisopropyl (3), *o*-methoxyphenyl (4), or tetrahydrofurfuryl (5), and tested as catalyst precursors for the syndiotactic polymerization of styrene (Table 3.2). The different structures of the alkoxyl ligands affected the activity slightly. When the polymerization was carried out in bulk, all the complexes (1-5) exhibited high activites, even at the low molar ratio of Al/Ti = 300. The active center might be described as $[CpTiMe]^+.[MAOX]^-.nMAO$. The $[CpTiMe]^+$ made up the core and the anion mass $[MAOX]^-.nMAO$ surrounded the core. The existence of the additional oxygen atom in the alkoxyl ligand stabilized the active species more effectively; this was reflected in the higher temperature of the maximum activities.

Table 3.2. Syndiotactic polymerization of styrene with MAO and various CpTiCl$_2$X complexes

Catalyst	[Ti] (mmol/L)	Al/Ti (mol/mol)	t_p (h)	Yield (g)	Activity ($\times10^{-6}$)	% SPS	T_m (°C)
1	0.42	2000	1.5	0.4565	3.50	95.1	260
	0.21	4000	13	0.3467	0.61	95.1	-
2	0.42	2000	2	0.6745	3.88	96.9	261
	0.21	4000	13	0.4855	0.86	96.8	-
3	0.42	2000	2	0.7015	4.03	97.3	260
	0.21	4000	13	0.5007	0.89	94.6	-
4	0.42	2000	1	0.3845	4.42	96.7	263
	0.21	4000	13	0.3740	0.66	95.0	-
5	0.42	2000	2	0.6390	3.67	97.1	261
	0.21	4000	13	0.3128	0.55	93.8	-

Activity = (g of PS)/[(mol of Ti) (mol of styrene) h]

Kaminsky *et al.* [62] investigated fluorinated half-sandwich complex of titanium, CpTiF$_3$. It showed an increase in activity of up to a factor of 50 compared to chlorinated complex. In a temperature range of 10-70°C the excess of methylaluminoxane (MAO) can be reduced to an Al/Ti molar ratio of 300. The highest melting point of 277°C can be obtained using pentamethylcyclopentadienyl titanium trifluoride Cp*TiF$_3$. This fluorinated complex affords polymers with a significantly higher molecular weight than with the chlorinated complex. Alkyl substitution of the cyclopentadienyl ligand can increase the activity. Schellenberg and Newman [63] found that polymerization activity of η^5-pentamethylcyclopentadienyl titanium trifluoride (Cp*TiF$_3$) in the presence of relatively low amount of methylalumoxane (Al/Ti molar ratio of 200) and triisobutylaluminum, is significantly increased by the addition of phenylsilane (molar ratios of phenylsilane/Cp*TiF$_3$ ranging from about 300/1 to 600/1). A prereaction of phenylsilane with the catalyst mixture shows a behavior that is strongly dependent on the storage time of the composition and the temperature. A storage time of about 16 h would cause the

polymerization conversion to reduce to about half of the original value. The results are discussed on the basis of a chain -transfer reaction with phenylsilane.

Rhodes *et al.* [64] synthesized and studied catalytic activity of several titanium (IV) complexes of the type $CpTi(NMe_2)_3$ [Cp = cyclopentadienyl (1), (dimethylaminoethyl)cyclopentadienyl (2), indenyl (3), and pentamethylcyclopentadienyl (4)] in the polymerization of olefins. Complexes (1) and (2) catalyzed the polymerization of ethylene in the presence of methylaluminoxane with a much higher activity than complex (3) or (4) of which has activity similar to that of $CpTiCl_3$. The preactivation of catalyst with trimethylaluminum (TMA) resulted in an increase in polymerization activities. Also, complexes (1) and (2) were successfully used as ethylene/1-hexene copolymerization catalysts, producing polymers with various amounts of 1-hexene incorporation, depending on the amount of 1-hexene in the feed mixture. Complex (1) likewise effectively polymerized styrene with a higher activity and higher syndiospecificity. Complexes (3) and (4) polymerized styrene with low syndiospecificity, whereas 2 produced only atactic polystyrene.

Kim *et al.* [65] synthesizesd titanatranes containing cyclopentadienyl ligands by the reactions of various kinds of trialkanolamines with $(C_5Me_4R)TiCl_3$ in the presence of triethylamine (Figure 3.3), all complexes show very high catalytic activity for the syndiospecific polymerization of styrene in the presence of modified methylaluminoxane (MMAO) cocatalyst (Table 3.3).

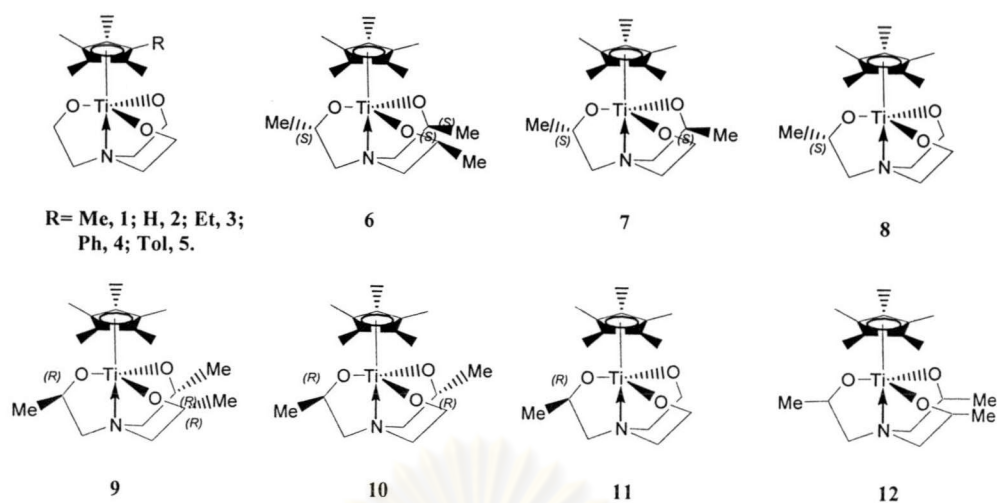R= Me, 1; H, 2; Et, 3; Ph, 4; Tol, 5.   6   7   8

9   10   11   12

Figure 3.3. New titanatranes.

Table 3.3. Styrene polymerization catalyzed by titanatranes/MMAO

Catalyst	Yield (g)	Activity ($\times 10^{-7}$)	Conversion (%)	T_m (°C)	%SPS	M_W	M_n	M_W / M_n
(η^5-C$_5$Me$_5$)TiCl$_3$	3.00	2.12	66	272.7	95.4	182,300	87,800	2.09
1	4.01	2.83	88	273.4	98.2	292,000	71,700	4.07
(η^5-C$_5$Me$_4$H)TiCl$_3$	1.50	1.06	33	260.4	86.7	15,300	8,300	1.85
2	3.25	2.29	71	261.9	96.8	43,200	22,500	1.92
(η^5-C$_5$Me$_4$Et)TiCl$_3$	0.72	0.51	16	265.9	40.3	25,300	9,600	2.62
3	1.46	1.03	32	274.1	98.3	65,700	34,600	1.90
(η^5-C$_5$Me$_4$Ph)TiCl$_3$	1.32	0.93	29	269.4	69.7	22,000	12,400	1.77
4	1.98	1.40	44	273.7	98.7	123,500	68,800	1.80
(η^5-C$_5$Me$_4$Tol)TiCl$_3$	0.59	0.42	13	260.1	32.2	30,300	11,400	2.65
5	1.17	0.83	26	271.8	97.5	133,600	74,600	1.79
6	2.23	1.57	50	273.9	98.7	31,400	17,100	1.84
7	2.31	1.63	51	273.6	98.4	33,700	18,500	1.82
8	1.92	1.35	42	273.3	98.5	34,000	18,900	1.80
9	2.61	1.84	57	274.8	98.8	31,600	17,200	1.84
10	2.29	1.61	50	275.4	99.0	33,400	17,900	1.86
11	1.83	1.29	40	273.6	98.8	34,100	17,200	1.98
12	0.92	0.65	20	273.5	97.4	135,800	48,400	2.81

Activity = (g of PS)/[(mol of Ti) (mol of styrene) h]

Wu *et al.* [66] investigated syndiotactic polymerization of styrene with cyclopentadienyltribenzyloxy titanium/methylaluminoxane (MAO) catalyst. The reaction conditions, e.g., the concentration of Ti, MAO, styrene, temperature and the content of retained trimethylaluminium (TMA) in MAO effected on the catalytic activity, syndiotacticity and molecular weight of the polymer. With the concentration of MAO = 0.17 mol/l, the catalyst exhibits higher activities. The catalytic activity increased with increase of the concentration of MAO, and reaches a maximum value at the concentration of MAO of 0.5 mol/l. The molecular weight of the polymer decreased and the molecular weight distribution became narrow with increasing of the MAO concentration. The concentration of MAO was necessary for activating the titanocene molecules and scavenging impurities. Additionally, the MAO acted as a chain transfer agent, so that the higher the MAO concentration used, the lower is the molecular weight of the polystyrene produced. The catalytic activity was directly proportional to the monomer concentration.

3.2   Supports

For industrial gas phase and slurry polymerization processes, however, heterogeneous catalyst systems are required. The catalyst support acts as a template in these particle growth processes and controls the size and morphology of the resulting polymer. In this respect the mechanical strength and fragmentability of the catalyst support should be in balance. Partial success has been achieved by using SiO_2, Al_2O_3, $MgCl_2$ as well as polymer resins as carriers. Drawbacks of these systems include leaching of the catalytically active sites or incomplete fragmentation of the carrier matrix. Complete fragmentation with exposure of new, polymerization active centers is necessary in order to improve productivity as well as polymer morphology. Inorganic supports for metallocenes, such as SiO_2, Al_2O_3, $MgCl_2$ show rigid and polar surface structure as opposed to polymer carriers.

Crosslinked polystyrene beads possess several of the attributes of an ideal catalyst support. They are unreactive to the metallocene cation, commercially available in different sizes and crosslinking densities, and amenable to numerous functionalization procedures utilizing both nucleophiles and electrophiles.

A particularly important property of lightly crosslinked beads is their ability to swell in organic solvents.

Xu *et al.* [67] prepared CpTiCl$_3$ on polymer supports with different hydroxyl contents for styrene polymerization. The supported catalysts exhibited high activity even at low Al/Ti ratios and increased the molecular weight of the products, indicating that polymer carriers could stabilize the active sites. The polymer obtained by supported catalysts had a high fraction of boiling *n*-butanone insoluble part and high melting temperatures, but ^{13}C NMR results showed that syndiotacticity decreased compared with that of polymer prepared with an unsupported catalyst. ESR study on the supported catalysts confirmed that the catalyst supported on the carrier dropped into the solution and formed active sites similar to those in the unsupported system when they reacted with methylaluminoxane. ^{13}C NMR analysis showed that the polymerization mechanism of the supported active sites was an active-site controlled mechanism instead of a chain-end controlled mechanism of the unsupported active sites.

Yu *et al.* [68] prepared poly(styrene-*co*-acrylamide)(PSAm)-titanium complexes (PSAm.Ti). The coordination number of acrylamide (Am) to Ti in the complexes is strongly dependent on Am content in PSAm, but not on [Am]/[Ti] ratio in the feed. The infrared and x-ray photoelectron spectra suggest that polymer-supported complexes possess the structure below:

$$\text{Ti} \longleftarrow \text{O}$$
$$\diagdown$$
$$\text{C} \text{---} \text{R}$$
$$\diagup$$
$$\text{H}_2\text{N}$$
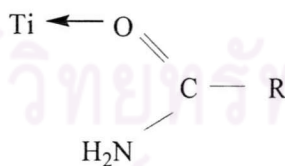
The catalytic activity is markedly affected by [Al]/[Ti] ratio in the complexes. ^{13}C NMR, IR, and DSC data indicate that polystyrene obtained with PSAm.Ti/MAO is highly syndiotactic. Use of Et$_3$Al and i-Bu$_3$Al in place of MAO gives atactic polystyrene. The activities of the various aluminum compounds used as the cocatalysts decrease in the order: MAO > Et$_3$Al > *i*-Bu$_3$Al The polymer-supported complexes show relatively high activity even after the complexes had been exposed to air for 19 h or higher polymerization temperature.

Hong *et al.* [69] used poly(styrene-*co*-divinylbenzene) beads supported *rac*-Ph$_2$Si(Ind)$_2$ZrCl$_2$ for ethylene polymerization using methylaluminoxane (MAO) as a cocatalyst. At a polymerization temperature below 100°C, the catalyst showed high activity to give polyethylene beads replicating the shape of the carrier. With increasing polymerization temperature up to 150 °C, the catalyst activity increased drastically but the spherical shape of polyethylene disappeared due to the melting.

Stock *et al.* [70] studied zirconocene dichloride/methylaluminoxane catalyst supported on a crosslinked polystyrene for gas phase or slurry process ethylene polymerization. This provides polymer supported zirconocene catalysts with a homogeneous distribution of active sites. The catalysts were shown to be highly active and to form spherical beads as proven by scanning electron microscopy.

Liu *et al.* [71] investigated the use of functional group bearing silica/poly (styrene-*co*-4-vinylpyridine) core-shell particles as a support for a zirconocene catalyst in ethylene polymerization (Figure 3.4). Several factors affecting the behavior of the supported catalyst and the properties of the resulting polymer, such as time, temperature, Al/N (molar ratio), and Al/Zr (molar ratio), were examined. The conditions of the supported catalyst preparation were important. The state of the supported catalyst played a decisive role in both the catalytic behavior of the supported catalyst and the properties of polyethylene. IR and X-ray photoelectron spectroscopy were used to follow the formation of the supports. The bulk density of the polyethylene formed was higher than that of the polymer obtained from homogeneous and polymer-supported Cp$_2$ZrCl$_2$ /methylaluminoxane catalyst systems.
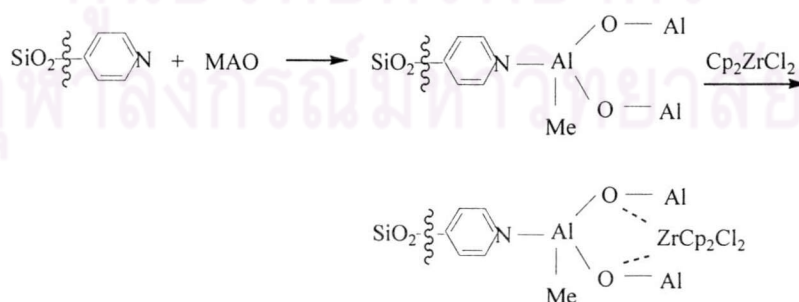

Figure 3.4. Structure of the core-shell-particle-supported catalyst.

Nenov *et al.* [72] prepared and tested a new catalyst system based on easily accessible crosslinked (by Diels-Alder reaction) polymeric supports, functionalized with nucleophilic polyethyleneoxide monomethylether (PEO-M). The metallocene-MAO complex is noncovalently bonded to the support. The polymerization of propylene and ethylene with $Me_2Si(2MeBenzInd)_2ZrCl_2$ is performed using this support. The resulting polymers have high molecular weights and melting points and narrow molecular distribution. Polypropylene is produced with 95% isotacticity similar to that from homogeneous catalysis. The productivities of up to 8600 for polypropylene and 1300 (kg polymer/mol. Zr. hour. bar) for polyethylene are comparably high. The product beads exhibit a good morphology.

Roscoe *et al.* [73] studied heterogeneous polyolefin catalysts based on metallocenium salts of weakly coordinating anions via a series of simple reactions from lightly crosslinked chloromethylated polystyrene beads (Figure 3.5). The polymer-supported catalysts have been used effectively for the polymerization of ethylene and propylene. Catalytic sites are distributed homogeneously throughout the polystyrene particles. The nonporous nature of these catalysts affords a high degree of control over the olefin uptake rate, avoiding problems of premature catalyst fragmentation that often plague high-surface-area heterogeneous catalysts based on highly reactive species. The dative interactions between the metallocene cation and the amine functionality of the support material are sufficient to prevent extraction under polymerization conditions to yield excellent particle morphology of the polyolefin produced.
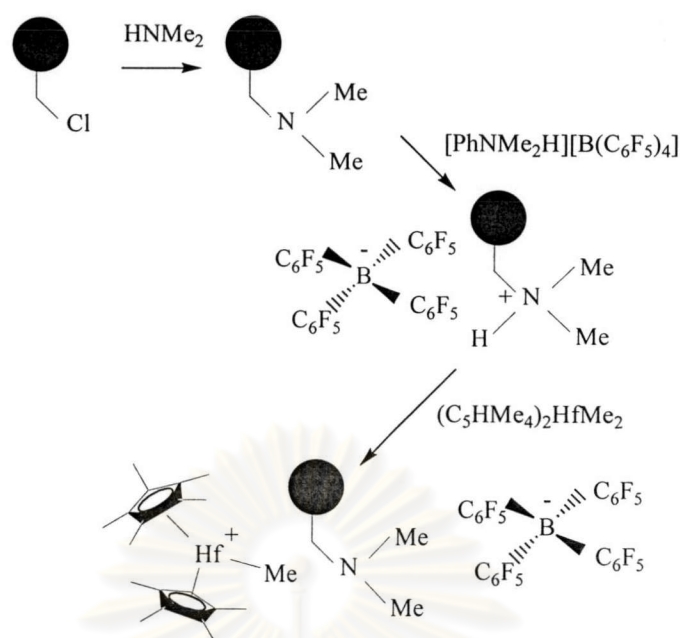
Figure 3.5. Sequential functionalization of chloromethylated polystyrene-DVB beads with a secondary amine, an acidic salt of the tetrakis(perfluorophenyl)boron anion, and a dimethylmetallocene.

Kishi *et al.* [74] prepared polymer supported borate complexes using poly (styrene-*co*-4-bromostyrene) and polystyrene-beads as carriers. These complexes were reacted with *rac*-Et[Ind]$_2$ZrCl$_2$ or Ph$_2$C[(Cp)Flu]ZrCl$_2$ in toluene, at a molar ratio of [Zr]/[B] = 1, to obtain polymer supported catalysts. Polymerizations of ethylene and propylene were conducted in the presence of Al(*i*-C$_4$H$_9$)$_3$. The insoluble catalyst prepared with polystyrene-beads as carrier displayed far less activities for both ethylene and propylene polymerizations, it was found that the shape of polyethylene obtained at 40 °C is a replica of the carrier particle.

Charoenchaidet *et al.* [75] investigated silica treated with tris(pentafluorophenyl)borane, B(C$_6$F$_5$)$_3$, to create borane-functionalized support, SiO$_2$-B(C$_6$F$_5$)$_3$ which was then used as a support and cocatalyst for the *in situ* activated dichloro-zirconocene (Cp$_2$ZrCl$_2$/TIBA) and dimethyl-zirconocene (Cp$_2$Zr(CH$_3$)$_2$) for ethylene polymerization. The surface modifications of SiO$_2$-B(C$_6$F$_5$)$_3$ were investigated by SEM-EDX, FTIR and XPS to determine the distribution of fluorine and boron atoms on the silica surface as a measure of the presence of B(C$_6$F$_5$)$_3$ and interaction with the siloxane groups of the silica support. Catalytic

performances were presented in the form of ethylene consumption rate profiles. All pre-activated systems showed activity decay. In contrast, the *in situ* activated systems either showed little or no activity decay. The presence of TIBA was adequate to make an active MAO-free catalyst system. The pre-activated and *in situ* activated metallocene systems produced polyethylene with slightly different molecular weight and molecular weight distribution (MWD ≈ 3). The bulk density of polyethylene product is highest for the *in situ* activated metallocenes, but there is no difference between the products of dichloro- and dimethyl-zirconocenes.

3.3 Copolymers

Kawabe and Murata [76] studied the polymerization of styrene and 4-methylstyrene with a half-metallocene type catalytic system composed of (trimethyl)pentamethylcyclopentadienyltitanium (Cp*TiMe$_3$) , trioctylaluminum (AlOct$_3$) , and tris(pentafluorophenyl)borane [B(C$_6$F$_5$)$_3$] at -25°C. The addition of AlOct$_3$ as a third component of the catalytic system is effective both to promote the syndiospecific polymerization and to inhibit the nonstereospecific polymerization. The use of AlOct$_3$ was also effective to eliminate the chain transfer reaction to alkylaluminum. The number-average molecular weights (M_n's) of the polymers increased proportionally with increasing monomer conversion. The molecular weight distribution (MWD) of polymer was narrow (1.1-1.5). It was thus concluded that the polymerizations of the styrenic monomers with Cp*TiMe$_3$/B(C$_6$F$_5$)$_3$/AlOct$_3$ catalytic system proceeded under living fashion at -25°C. The ^{13}C NMR analysis clarified that each of the homopolymers and random copolymers possessed highly syndiotactic structure.

Seppala *et al.* [77] studied the copolymerization of ethylene and styrene using the catalytic system CpTiCl$_3$–methylaluminoxane. The polymerization product was composed of polyethylene and syndiotactic polystyrene. No ethylene-styrene copolymer was detected. The composition of the product was dependent on the polymerization conditions. The catalystic activity was highest at polymerization temperature of 30°C and Al/Ti molar ratio of 1500. Styrene content of the product was highest at polymerization temperature of 50°C and Al/Ti molar ratio of 1500. The

formation of separate polymer fractions might indicate a different polymerization mechanism for the two monomers, the presence of more than one active species in the catalyst, one producing polyethylene and the other syndiotactic polystyrene.

Pappalardo *et al.*[78] investigated the copolymerization of ethylene and styrene using the catalytic system $Cp*Ti(CH_2Ph)_3-B(C_6F_5)_3$. Alternating ethylene-styrene copolymer was obtained, together with some polyethylene and syndiotactic polystyrene, from which the former could be seperated by solvent extraction. NMR analysis of suitably C^{13} -enriched end groups shows that the regiospecificity of styrene insertion in the initiation step is largely secondary.

Chien and He [79] studied supported catalyst for fluidized bed polymerization process by reacting macroporous SiO_2 first with MAO and then with $Et[Ind]_2ZrCl_2$. It contains 0.60 wt% of Zr and an [Al]/[Zr] molar ratio of 50. This catalyst produces homogeneous ethylene/propylene copolymers with truly random copolymerization behaviors and requires a total [Al]/[Zr] molar ratio of only 670. Several times larger amount of MAO would be required to achieve the same copolymerization activity for the $Et[Ind]_2ZrCl_2$/MAO catalyst in solution. This random copolymerization is independent of catalyst concentration and composition. Activation of the supported catalyst with *i*-butylaluminoxane, tri-*i*-butylaluminoxane, or trimethylaluminum resulted in lower activity and copolymers having high ethylene content and crystallinity.